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Patent Assignee: 000005290
Furukawa Denki Kogyo Kabushiki Kaisha
[Furukawa Electrical Industries Corporation]
6-1 Marunouchi 2-chome, Chiyoda-ku, Tokyo-to

Inventor: Kazuhiko Matsuzaki
c/o Furukawa Denki Kogyo Kabushiki Kaisha
[Furukawa Electrical Industries Corporation]
6-1 Marunouchi 2-chome, Chiyoda-ku, Tokyo-to

Inventor: Yukio Urayoshi
c/o Furukawa Denki Kogyo Kabushiki Kaisha
[Furukawa Electrical Industries Corporation]
6-1 Marunouchi 2-chome, Chiyoda-ku, Tokyo-to

Inventor: Katsuki Koyama
c/o Furukawa Denki Kogyo Kabushiki Kaisha
[Furukawa Electrical Industries Corporation]
6-1 Marunouchi 2-chome, Chiyoda-ku, Tokyo-to

Title of the Invention: Aluminium alloy for resin-coated can bodies and resin-coated aluminium alloy sheets for can bodies

Summary

Purpose

The invention proposes resin-coated Al alloy sheets for can bodies whereon a resin film is coated with good close adhesion.

Solution means

The invention proposes resin-coated Al alloy sheets for can bodies comprising 0.1~0.5 mm thick Al alloy sheets containing 0.30~0.80wt%Si, less than 0.70wt%Fe, 0.01~0.50wt%Cu, 0.40~1.50wt%Mn, 0.80~6.00wt%Mg, 0.001~0.15wt%Ti, and 0.10~0.40wt%Zn, whereon a resin film is coated on one surface or both surfaces of said Al alloy sheets.

Effect

Said Mg and Si crystallize out as Mg_2Si . In the surface zone of the aluminium alloy sheets where said Mg_2Si crystallites are present, the aluminium is depleted. For this reason, in the aluminium oxide film formed on said alloy surface, said aluminium depletion zone forms depressions, and the resin film is coated with good close adhesion through these depressions exhibiting an anchoring effect in such a way as to obtain high-quality can bodies without any exfoliation even during can forming.

Claims

Claim 1. Aluminium alloy for resin-coated can bodies, characterized in that it contains 0.30~0.80wt%Si, less than 0.70wt%Fe, 0.01~0.50wt%Cu, 0.40~1.50wt%Mn, 0.80~6.00wt%Mg, 0.001~0.15wt%Ti, and 0.10~0.40wt%Zn and consists of bal. Al and unavoidable impurities.

Claim 2. Resin-coated aluminium alloy sheets for can bodies, characterized in that they comprise 0.1~0.5 mm thick Al alloy sheets containing 0.30~0.80wt%Si, less than 0.70wt%Fe, 0.01~0.50wt%Cu, 0.40~1.50wt%Mn, 0.80~6.00wt%Mg, 0.001~0.15wt%Ti, and 0.10~0.40wt%Zn and consist of bal. Al and unavoidable impurities, and a resin film is coated on one surface or both surfaces of said Al alloy sheets.

Claim 3. Resin-coated aluminium alloy sheets for can bodies as claimed in claim 2, characterized in that one surface or both surfaces of said Al alloy sheets are subjected to etching treatment, and a resin film is coated thereon.

Claim 4. Resin-coated aluminium alloy sheets for can bodies as claimed in claim 2, characterized in that one surface or both surfaces of said Al alloy sheets are subjected to etching treatment, chemical conversion film treatment is performed thereon, and a resin film is further coated thereon.

Claim 5. Resin-coated aluminium alloy sheets for can bodies as claimed in any one of claims 2, 3, and 4, characterized in that a high-volatility lubricant is coated on said resin film.

Detailed Explanation of the Invention

[0001]

Industrial Application Field

This invention relates to an aluminium alloy for resin-coated can bodies whereon a resin film is coated with good close adhesion and to resin-coated aluminium alloy sheets for can bodies whereon a resin film is coated with good close adhesion.

[0002]

Prior Art

The bodies of beverage cans are normally formed through the processes of drawing and ironing (DI working) being consecutively performed on thin aluminium or steel sheets. During said DI working, however, large quantities of lubricant are used, thus raising the problem of adequate drainage treatment. As a remedial measure, a resin film with abundant lubricity has been coated on the thin steel sheets, resulting in development of the downgauged redrawn laminated can.

[0003]

Problems to be Solved by the Invention

Aluminium offers better recyclability than steel and is therefore used in the manufacture of beverage cans. Through the surface being readily susceptible to oxidation, however, the surface only ensures poor adhesion with the resin film, which is apt to exfoliate during can forming (DI working, etc), and the aluminium laminated can has therefore not seen any practical applications. In this context, the authors of this invention, having been engaged in intensive research efforts intended to achieve improved close adhesion between the aluminium alloy sheets and resin film, have discovered that aluminium alloy sheets wherein Mg_2Si crystallites are dispersed in appropriate quantity provide improved close adhesion with the resin film, and have proceeded to elaborate this invention. The purpose of this invention is to propose an aluminium alloy for resin-coated can bodies whereon a resin film is coated with good close adhesion and resin-coated aluminium alloy sheets for can bodies whereon a resin film is coated with good close adhesion.

[0004]

Means of Solving the Problems

Claim 1 of this invention relates to an aluminium alloy for resin-coated can bodies, characterized in that it contains 0.30~0.80wt%Si, less than 0.70wt%Fe, 0.01~0.50wt%Cu, 0.40~1.50wt%Mn, 0.80~6.00wt%Mg, 0.001~0.15wt%Ti, and 0.10~0.40wt%Zn and consists of bal. Al and unavoidable impurities.

[0005]

Claim 2 of this invention relates to resin-coated aluminium alloy sheets for can bodies, characterized in that they comprise 0.1~0.5 mm thick Al alloy sheets containing 0.30~0.80wt%Si, less than 0.70wt%Fe, 0.01~0.50wt%Cu, 0.40~1.50wt%Mn, 0.80~6.00wt%Mg, 0.001~0.15wt%Ti, and 0.10~0.40wt%Zn and consist of bal. Al and unavoidable impurities, and a resin film is coated on one surface or both surfaces of said Al alloy sheets.

[0006]

Claim 3 of this invention relates to resin-coated aluminium alloy sheets for can bodies as claimed in claim 2, characterized in that one surface or both surfaces of said Al alloy sheets are subjected to etching treatment, and a resin film is coated thereon.

[0007]

Claim 4 of this invention relates to resin-coated aluminium alloy sheets for can bodies as claimed in claim 2, characterized in that one surface or both surfaces of said Al al-

loy sheets are subjected to etching treatment, chemical conversion film treatment is performed thereon, and a resin film is further coated thereon

[0008]

Claim 5 of this invention relates to resin-coated aluminium alloy sheets for can bodies as claimed in any one of claims 2, 3, and 4, characterized in that a high-volatility lubricant is coated on said resin film.

[0009]

Configuration of Invention Embodiment

In the aluminium alloy according to this invention, Mg_2Si crystallizes out in appropriate quantity inside the Al matrix. When these Mg_2Si crystallites are present on the surface of the aluminium alloy sheets, the aluminium is depleted in this zone. For this reason, in the aluminium oxide film formed on said alloy surface, said aluminium depletion zone forms depressions, and the resin film is coated with good close adhesion through these depressions exhibiting an anchoring effect in such a way as to obtain high-quality can bodies without any exfoliation even during can forming.

[0010]

The alloying elements of the aluminium alloy according to this invention are explained below. Si reacts with Mg to crystallize out as Mg_2Si in such a way as to improve close adhesion of the resin film as described above. Specification of the Si content within the 0.30~0.80wt% range is due to the fact that, at a content of less than 0.30 wt%, no such anchoring effect is adequately obtained, whereas, at a content exceeding 0.80 wt%, the amount of Mg in solid solution decreases in such a way as to reduce the strength. If Mg is added to compensate for the reduced amount of Mg in solid solution, coarse Mg_2Si crystallites crystallize out in such a way as to reduce the can formability.

[0011]

Fe is included as an impurity in the Al base metal. Specification of the Fe content as less than 0.70 wt% is due to the fact that, at a content of more than 0.70 wt%, coarse Al-Mn-Fe crystallites are formed in such a way as to reduce the can formability.

[0012]

Cu contributes to strength improvement and also improves the workability during manufacturing through refining the grain size. Specification of the Cu content within the 0.01~0.50 wt% range is due to the fact that, at a content of less than 0.01 wt%, no such effect is adequately obtained, whereas, at a content exceeding 0.50 wt%, coarse Cu-containing crystallites are formed in such a way as to reduce the can formability.

[0013]

Mn also contributes to strength improvement. Specification of the Mn content within the 0.40~1.50 wt% range is due to the fact that, at a content of less than 0.40 wt%, no such effect is adequately obtained, whereas, at a content exceeding 1.50 wt%, this effect becomes saturated, and coarse crystallites, such as Al-Mn, Al-Mn-Fe, etc, are formed in such a way as to reduce the can formability.

[0014]

Mg also contributes to strength improvement. Specification of the Mg content within the 0.80~6.00 wt% range is due to the fact that, at a content of less than 0.80 wt%, the Mg_2Si crystallites are reduced, and no such effect is adequately obtained, whereas, at a content exceeding 6.00 wt%, the workability during manufacturing and the can formability are reduced. At a high Si content, the strength is here preferably adjusted by increasing the Mg content.

[0015]

Ti enhances the workability during manufacturing by refining the casting structure. Specification of the Ti content within the 0.001~0.15 wt% range is due to the fact that, at a content of less than 0.001 wt%, no such effect is adequately obtained, whereas, at a content exceeding 0.15 wt%, coarse Ti-containing crystallites increase in such a way as to reduce the can formability.

[0016]

Zn contributes to strength improvement. It also refines crystallites, such as Mg_2Si , etc, in such a way as to enhance their anchoring effect. Specification of the Zn content within the 0.10~0.40 wt% range is due to the fact that, at a content of less than 0.10 wt%, no such effect is adequately obtained, whereas, at a content exceeding 0.40 wt%, this effect becomes saturated, and the can formability is reduced.

[0017]

The aluminium alloy as claimed in claim 1 is easily worked into a sheet material by the normal method of semi-continuous casting → ingot homogenization → hot rolling → cold rolling (with intermediate annealing being performed where necessary).

[0018]

The resin-coated aluminium alloy sheets for can bodies as claimed in claim 2 comprise a sheet material obtained through said aluminium alloy being worked by the normal method. On the surface of the aluminium alloy sheets, Mg_2Si crystallites are exposed in appropriate quantity. In the zone where these Mg_2Si crystallites are present on the surface of the aluminium alloy sheets, the aluminium is depleted. For this reason, in the aluminium oxide film formed on said alloy surface, said aluminium depletion zone forms depressions, and the resin film is coated with good close adhesion through these depressions exhibiting an anchoring effect in such a way as to obtain high-quality can bodies without any exfoliation even during can forming. Specification in this invention of the thickness of said aluminium alloy sheets within the 0.1~0.5 mm range is due to the fact that, at a thickness of less than 0.1 mm, the strength required for can bodies is not adequately obtained, whereas, at a thickness exceeding 0.5 mm, the strength is unnecessarily increased in a way that is uneconomic.

[0019]

In the resin-coated aluminium alloy sheets for can bodies as claimed in claim 3, one surface or both surfaces of said Al alloy sheets are subjected to etching treatment in such a way that the Mg_2Si crystallites exposed on the surface are discretely arranged to form discrete holes, and the anchoring effect of the Mg_2Si crystallites is thereby vastly improved.

[0020]

Available resin film coating methods include the hot pressure deposition method involving the resin film being heated at a temperature above its melting point and the method involving the use of an adhesive. By the former method, the resin film is anchored in the Mg_2Si crystallites. By the latter method, the adhesive is so anchored. By both methods, the resin film is coated on the aluminium alloy surface with good close adhesion.

[0021]

The lubricity of the coated resin film is strongly affected by factors such as the degree of resin film granulation, the degree of adhesive hardening, etc. Adequate consideration must therefore be given to temperature control during and after resin film coating.

[0022]

In this invention, the resin film preferably comprises a polyester, polyolefin, or polyamide resin film with little release of noxious environmental hormones, such as bisphenol A.

[0023]

In this invention, the applied etching treatment, in addition to enhancing the anchoring effect of the Mg_2Si crystallites by forming discrete holes of said crystallites, also enhances close adhesion of the resin film at the point when surface contamination or the oxide film is removed.

[0024]

The aluminium alloy sheets as claimed in claim 4, after etching treatment, are subjected to chemical conversion film treatment whereby close adhesion of the resin film is vastly improved. Said chemical conversion film treatment is performed by normal methods such as the MBV method (alkali chromate system), Arotin method (chromate system, phosphate-chromate system), boehmite method (oxide film system), etc.

[0025]

In claim 5 of this invention relating to aluminium alloy sheets as claimed in any one of claims 2~4, a high-volatility lubricant is coated on the resin film to enhance can formability. High-volatility lubricants, through having inferior lubricity, are generally little used in isolation. However, such a high-volatility lubricant is used here to assist resin film lubricity, the effect achieved being satisfactory. Since said lubricant is highly volatile, there is no need for any cleaning after DI working.

[0026]

Embodiment examples

This invention is explained in more detail below with reference to a number of embodiment examples.

Embodiment example 1

Resin-coated aluminium alloy sheets for can bodies were prepared through aluminium alloy ingots within the specified composition range of this invention listed in Table 1 (No. A~G) being used to manufacture 0.3 mm thick rolled sheets by hot rolling and cold rolling and through a 15 μm thick thermoplastic polyethylene terephthalate resin film being coated thereon by means of a low melting point adhesive. This coated resin film was then heated for a short time at a temperature just above the melting point (270°C) and water-cooled to obtain a non-crystallized state.

[0027]

Reference example 1

Resin-coated aluminium alloy sheets for can bodies were prepared in the same way as for embodiment example 1 except for the aluminium alloy ingots being used outside the specified composition range of this invention listed in Table 2 (No. H~R).

[0028]

Various properties -- the strength (tensile strength, proof stress), can formability, and close adhesion of the resin film -- of the resin-coated aluminium alloy sheets for can bodies manufactured by the methods described for embodiment example 1 and reference example 1 were investigated. Tables 3 and 4 list the results obtained. The strength was measured to JIS H4000 specifications. The can formability was evaluated according to the degree of cracking that occurred during continuous forming of 350 ml size cans by DI working (inside diameter of 66 mm) → four-stage necking → flanging. The can formability was evaluated as very good (●) when no fractured can bodies or flange cracks were present among 1000 manufactured cans, good (O) when less than 50 cans showed flange cracks, fairly poor (Δ) when more than 50 and less

than 200 cans showed flange cracks, and poor (X) when more than 200 cans showed flange cracks. To evaluate close adhesion of the resin film, the states of resin film exfoliation during forming of said cans were observed. Close adhesion of the resin film was evaluated as good (O) when no cracking occurred and poor (X) when cracking occurred.

[0029]

Table 1

	Alloy No.	Si	Fe	Cu	Mn	Mg	Ti	Zn	Al
Within specified composition range of this invention	A	0.31	0.28	0.22	0.75	1.12	0.03	0.12	bal.
	B	0.78	0.22	0.23	0.66	1.20	0.08	0.32	bal.
	C	0.61	0.60	0.44	0.43	0.90	0.12	0.18	bal.
	D	0.59	0.52	0.19	1.48	0.99	0.03	0.24	bal.
	E	0.48	0.66	0.21	1.12	0.83	0.03	0.28	bal.
	F	0.62	0.41	0.09	0.48	2.75	0.03	0.34	bal.
	G	0.66	0.33	0.14	0.44	5.12	0.04	0.38	bal.

Note. Unit: wt%.

[0030]

Table 2

	Alloy No.	Si	Fe	Cu	Mn	Mg	Ti	Zn	Al
Outside specified composition range of this invention	H	0.19	0.32	0.08	0.44	0.82	0.03	0.32	bal.
	I	0.88	0.20	0.20	1.18	0.82	0.04	0.32	bal.
	J	0.67	0.82	0.31	0.68	2.31	0.03	0.33	bal.
	K	0.40	0.23	0.73	1.20	3.12	0.03	0.32	bal.
	L	0.49	0.22	0.39	0.15	0.85	0.02	0.33	bal.
	M	0.42	0.29	0.40	1.78	0.93	0.03	0.34	bal.
	N	0.47	0.31	0.12	0.90	0.52	0.04	0.31	bal.
	O	0.51	0.38	0.14	0.45	7.12	0.03	0.33	bal.
	P	0.42	0.41	0.18	0.44	5.25	0.23	0.32	bal.
	Q	0.46	0.23	0.24	1.33	2.24	0.03	0.08	bal.
	R	0.43	0.30	0.28	1.10	2.50	0.06	0.52	bal.

Note. Unit: wt%.

[0031]

Table 3

Classification	Sample No.	Alloy No.	Strength		Can formability		Close adhesion of resin film	
			Tensile strength, MPa	Proof stress, MPa	DI working	Opening expansion	DI working	Necking
Embodiment examples	1	A	291	257	●	●	O	O
	2	B	288	255	●	O	O	O
	3	C	289	256	●	O	O	O
	4	D	296	262	●	●	O	O
	5	E	295	260	●	●	O	O
	6	F	286	254	●	●	O	O
	7	G	325	282	O	●	O	O
Reference examples	8	H	273	246	●	Δ	X	X
	9	I	282	251	Δ	Δ	O	O

Note: Opening expansion: after four-stage necking → flanging.

[0032]

Table 4

Classification	Sample No.	Alloy No.	Strength		Can formability		Close adhesion of resin film	
			Tensile strength, MPa	Proof stress, MPa	DI working	Opening expansion	DI working	Necking
Reference examples	10	J	286	253	Δ	X	O	O
	11	K	291	263	X	-	O	O
	12	L	267	233	●	X	O	O
	13	M	293	266	X	-	O	O
	14	N	252	231	●	O	O	X
	15	O	251	290	X	-	O	O
	16	P	349	293	X	-	O	O
	17	Q	290	262	●	O	O	X
	18	R	318	279	Δ	Δ	O	O

Note: Opening expansion: after four-stage necking → flanging.

[0033]

As made clear by Tables 3 and 4, embodiment examples No. 1~7 satisfy the strength required for can bodies (a proof stress of more than 250 MPa) and also show superior can formability and close adhesion of the resin film. On the other hand, reference example No. 8, because of its low Si content, and No. 14, because of its low Mg content, both have a deficiency of Mg_2Si crystallites. No. 17, because of its low Zn content, further shows poor refinement of the Mg_2Si crystallites. In each case, close adhesion of the resin film is poor, resulting in reduced can formability. No. 14 also has a low proof stress. No. 9, because of its high Si content, has a reduced amount of Mg in solid solution, and No. 12, because of its low Mn content, has a low proof stress. No. 10, because of its high Fe content, No. 11, because of its high Cu content, No. 13 because of its high Mn content, No. 15 because of its high Mg content, No. 16 because of its high Ti content, and No. 18 because of its high Zn content, each contain coarse crystallites and show reduced can formability (DI workability and/or opening expandability).

[0034]

Embodiment example 2

Resin-coated aluminium alloy sheets for can bodies were prepared by the same method as described for embodiment example 1 through aluminium alloy ingots within the specified composition range of this invention listed in Table 1 being used to manufacture 0.3 mm thick rolled sheets by hot rolling and cold rolling. These rolled sheets were subjected to etching treatment (alkali pickling or acid pickling) on both surfaces and were the same as the rolled sheets in embodiment example 1 except for a 15 μm thick thermoplastic polyethylene terephthalate resin film being additionally coated thereon by means of a low melting point adhesive. Said alkali pickling was performed through the aluminium alloy sheets being immersed for 30 seconds in aqueous 1 wt% NaOH solution at 60°C. Acid pickling was performed through the aluminium alloy sheets being immersed for 30 seconds in a mixture of 75 vol% phosphoric acid and 25 vol% sulphuric acid at 100°C.

[0035]

Embodiment example 3

Resin-coated aluminium alloy sheets for can bodies were prepared by the same method as described for embodiment example 1 through the 0.3 mm thick rolled sheets being subjected to alkali pickling or acid pickling except for being additionally

subjected to phosphate-chromate treatment (with an amount of deposited Cr of 20 mg/mm²) or boehmite treatment thereon. Said boehmite treatment was performed through the aluminium alloy sheets being exposed for 5 minutes to water vapour at 105°C containing 3 wt% ammonia. An AlO₃.H₂O film with a thickness of around 0.2 µm was formed.

[0036]

Resin-coated aluminium alloy sheets for can bodies prepared for embodiment examples 2 and 3 were subjected to DI working and retort treatment, and close adhesion of their resin film was then investigated. Close adhesion of the resin film after DI working was evaluated by the occurrence rate ($n = 10^6$) of resin film flaws. Retort treatment was performed through the sample and tap water being placed in a sealed container and the latter being heated and held at 125°C x 30 minutes. Close adhesion of the resin film was evaluated on the basis of observations as to whether or not the resin film exfoliated during heating and holding noted above. Close adhesion of the resin film was evaluated as very good (●) when no cracks were present per each 100 manufactured cans, good (O) when 3 or more cans showed exfoliation, and poor (X) when 4 or more cans showed exfoliation. Table 5 lists the results obtained. For reference purposes, an alloy sample not receiving any surface treatment (No. 24) and a low-Si alloy sample (H) receiving etching treatment and chemical conversion film treatment (No. 25) were also similarly investigated.

[0037]

Table 5

Classification	Sample No.	Alloy No.	Etching (pickling)	Chemical conversion film	Close adhesion of resin film	
					Flaw rate during DI working	After retort treatment
Embodiment examples	19	G	Alkali	-----	7 ppm	O
	20	G	Acid	-----	8 ppm	O
	21	G	Acid	Phosphate-chromate system	3 ppm	O
	22	G	Alkali	Phosphate-chromate system	1 ppm	O
	23	G	Alkali	Oxide film system	2 ppm	O
Reference examples	24	G	None	None	850 ppm	X
	25	H	Alkali	Phosphate-chromate system	120 ppm	X

[0038]

As made clear by Table 5, embodiment examples No. 19~23 each have a low flaw rate during DI working, and close adhesion of their resin film after retort treatment is also good. On the other hand, reference example No. 24, through not receiving any etching treatment or chemical conversion film treatment, and No. 25, because of its low Si content, each have reduced close adhesion of their resin film.

[0039]

Resin-coated aluminium alloy sheets for can bodies prepared for embodiment example 3 were subjected to can forming through a high-volatility lubricant (low melting point wax) being coated on the surface of the aluminium alloy sheets, and close adhesion of the resin film after can forming and close adhesion of the resin film after retort treatment were investigated. Close adhesion of the resin film after retort treatment

was evaluated in much the same way as for embodiment example 3. Table 6 lists the results obtained.

[0040]

Table 6

Classification	Sample No.	Alloy No.	Etching (pickling)	Chemical conversion film	Close adhesion of resin film	
					Flaw rate during DI working	After retort treatment
Embodiment examples	26	G	Acid	Phosphate-chromate system	0 ppm	•
	27	G	Alkali	Phosphate-chromate system	0 ppm	•
	28	G	Alkali	Oxide film system	0 ppm	•

[0041]

As made clear by Table 6, embodiment examples No. 26~28, through having a high-volatility lubricant coated on the resin film, have a reduced frictional resistance of the resin film, with each one showing very good close adhesion of the resin film. This lubricant, through being highly volatile, vaporizes spontaneously and therefore requires no cleaning.

[0042]

The foregoing explains the case of the resin film being coated by means of an adhesive, but this invention achieves much the same effect when the resin film is coated by hot pressure deposition.

[0043]

Effect of the Invention

As described above, the aluminium alloy according to this invention contains Si, Fe, Cu, Mn, Mg, Ti, and Zn in appropriate quantities. Said Mg and Si crystallize out as Mg_2Si . In the surface zone of the aluminium alloy sheets where said Mg_2Si crystallites are present, the aluminium is depleted. For this reason, in the aluminium oxide film formed on said alloy surface, said aluminium depletion zone forms depressions, and the resin film is coated with good close adhesion through these depressions exhibiting an anchoring effect in such a way as to obtain high-quality can bodies without any exfoliation even during can forming. When the aluminium alloy sheets are subjected to etching treatment in such a way that the Mg_2Si crystallites exposed on the surface are discretely arranged to form discrete holes, the anchoring effect of the Mg_2Si crystallites is thereby vastly improved. When chemical conversion film treatment is performed after etching treatment, close adhesion of the resin film is also improved. When a high-volatility lubricant is coated on the resin film, there is no exfoliation of the resin film whatever, and can formability is substantially improved. Said lubricant, through being highly volatile, requires no cleaning and does not impair productivity. The invention thus confers an industrially significant effect.

F terms (ref.)

4F100 AB10A AB31A AK01B AK01C
AK42 BA03 BA05 BA08 BA10B
BA10C BA26 CA30E EJ51A
EJ68D EJ68E GB16 JL11
JM02D JM02E
4K026 AA09 AA22 BA07 BA08 BB06
BB10 CA16 CA36 EA08 EA10
EA12 EB11
4K053 PA10 PA12 RA15 RA18 RA22
TA06 TA07 ZA10
4K057 WA05 WA07 WB05 WB11 WE03
WE04 WE22 WK05 WK07 WN10